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Progress in research of comprehensive utilization of nonmetallic materials from waste printed circuit boards

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Abstract

The progress in current research in and abroad on recycling and reuse of nonmetallic materials from waste circuit boards was introduced, and technical principle and research situation of tradition techniques adopted for resource modification, including energy recovery techniques, solution recovery techniques, supercritical techniques, physical recovery techniques and pyrolysis techniques were discussed in details in this paper. And finally, it is concluded that comprehensive use of various methods is the tendency for recycling non-materials from waste circuit boards after exploring disadvantages and advantages of these five approaches.

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Nonmetallic materials from waste circuit boards refer to the remaining materials[1] after copper and other metals are separated from waste circuit boards through physical method, chemical method and combination of other methods, which take up more than 60% [2]of the circuit boards. They are mainly comprised of epoxy resin, brominated flame retardants, glass fiber, as well as cross linking agent, cross linking accelerator agent and so on[2, 3]. China, as the world's largest producer of printed circuit boards [4], and scraps most in the world, needs to dispose of more than 500,000 tons of PCBs[4, 5]. Namely, we need to process more than 300,000 tons of nonmetallic materials from waste circuit boards. The recycling of printed circuit boards currently focused on metal materials due to the low reuse values of nonmetallic materials and difficulties in the procedure of recycling [6].

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In the developed countries, including America and European countries, current recovery system is more perfect, main recycling methods adopted are energy recovery and physical recovery method, and processing enterprises in these areas enjoy a variety of subsidies and preferential policies [1, 7].

However, main methods of processing nonmetallic materials from circuit boards are still landfill and incineration in China [8, 9] , but safe landfill and incineration disposal sites which are in line with environmental protection requirements are still limited and the cost of processing is relatively high [1], which results in that the proportion of the companies disposing nonmetallic materials from waste circuit boards with environment-friendly method far lags behind that in developed countries. After refining valued metals, many small and medium enterprises in China just simply piled and buried remaining materials or even were burnt in open, which causes serious harm to environment and human health [9]. How to handle a huge amount of waste and hard-processing nonmetallic materials from circuit boards has become an important issue to environment in China. So, technical principles and current application situation of traditional methods for disposing and recycling nonmetallic materials from circuit boards, including energy recovery techniques, solution recovery techniques, supercritical techniques, physical recovery techniques and pyrolysis technology were introduced in this paper.

1. Energy recovery technique

Epoxy resin contains elements of C, H, O, and energy can be obtained by burning. Thermal recycling of nonmetallic materials from circuit boards is an eco-efficient waste management options available for end-of-life WEEE items[10]. Because the nonmetallic materials from waste circuit boards contain inorganic reinforcing material of glass fiber, the average calorific value is lower than the average plastic 40MJ/kg [1, 11]. So, the nonmetallic materials from circuit boards are usually mixed with municipal solid waste for heat value. Improper operation of the incineration process can easily produce dioxin and other toxic and hazardous substances [12] because the nonmetallic materials contain halogenated flame retardants. Thus, incineration of waste nonmetallic materials should normally be carried out in high-temperature incinerators, which must be equipped with flue gas treatment systems[1].

2. Solution recovery technique

Solution recovery method uses organic or inorganic solvents to decompose the cross linked network polymer matrix in PCB board, or hydrolysis into low molecular weight linear organic compounds, so components in the composite are easy to be separated and recovered. The current study of recycling of epoxy resin using solution method is relatively less [13]. Dang cured glass fiber reinforced bisphenol F type epoxy resin cured with diamino diphenyl methane (DDM) [14]. It was concluded that the approach was applicable to BPF/DDM epoxy resin, and potentially to all of amine cured epoxy resin. Flexural strength of the recycled resin was higher than that of virgin resin until the content of the neutralized extract, which was available from degradation of BPF/DDM epoxy resin, was less than 30 wt% of the original resin.

Hitachi Chemical Co., placed discarded circuit boards in the treating solution containing organic solvents and alkali metal. Under the conditions of increased pressure and high temperature (250 ℃), epoxy resin is biodegradable and chemical materials are obtained [15]. Ma used nitric acid as solvent for recycling epoxy resin with a concentration of 15.37%. The optimal conditions for recovering epoxy resin are as follows: reaction temperature 80 °C, reaction time 3 h, the concentration of nitric acid 8 mol / L, the ratio of the quality of waste circuit boards to volume of nitric acid 10g: 50mL [16].

3. Supercritical technique

Supercritical fluid technique uses supercritical fluid to destroy the epoxy adhesive layer in the printed circuit board and take away the decomposed small molecules, which can completely separate the layers of the printed circuit board from each other, so as to recycle the different components of the circuit boards [9]. Chien[17] and his team used the supercritical water oxidation technique to process waste circuit boards. This was done by adding hydrogen peroxide and lye to make the matrix resin completely decomposed and create a principal component-the residue of copper oxide. Wang [18] and his team used supercritical ethanol as extraction solvent. The average extraction ratio was over 90%, and the average adhesive ratio was below 5%. Supercritical fluid CO2 is able to destroy the adhesive effect in epoxy layer for separating different material layers in circuit boards. CO2, with mild critical performance, excellent security, high solubility, environmental friendliness, low price and stable chemical properties, is a kind of extraction solvent most studied[19]. By applying supercritical CO2, more than 80% in quality of original materials can be recovered and the content of metals and glass fiber is higher[20-23].

4. Physical recovery technique

4.1. Obtaining inorganic materials

4.1.1. Obtaining activated carbon

Take the nonmetallic separate matter in the wasted printed circuit boards as the precursor, after the process of pyrolysis, molding, carbonization and steam activation, to obtain granular activated carbon. Yang [24] and his team found that when the optimal activation time period was three hours, the surface area of the activated carbon was 1, 019 m2/g, while the iodine adsorption value was 788 mg/g.

4.1.2 Obtaining construction materials

Nonmetallic materials from waste circuit boards can be added into construction materials as filler，such as producing roadbed materials and cement mortar fillers, and so on[1].

(1) Cement mortar

Nonmetallic materials was added into cement mortar, both weight and compressive strength of cement mortar were observed to be recovered with aging[25]. If particle size of the nonmetallic materials is larger than 0.08mm and water leaching expansion ratio is higher than 2.0%, performance of the cement obtained will be better than that of standard cement[1].

(2) Asphalt modified additives

Yu[26] et al used nonmetallic materials as asphalt additives. When the temperature stays at 180℃ while modifying nonmetallic materials into asphalt, the comprehensive conditions of consolidation of penetration and softening point are the best; and when the optimal sharing time period reaches 1 h, the consolidation of penetration and softening point are also the best.

(3) Fiber reinforced polymer composite covers, construction templates

PCB nonmetallic materials have excellent compatibility with FRP composites, so it can directly replace some calcium carbonate [2]. PCB nonmetallic materials can also be added to plaster concrete as

filling materials to obtain various nonmetallic fillers, such as bricks and composite boards. However, both cement and sand are very cheap, so to replace nonmetallic materials is of low economic benefit, and these filler materials are just at the stage for laboratory research, less in application[4,27].

4.2. Obtaining composite materials

Composite materials are currently one of the brightest fields in application and development among the field of materials[1], and also main product of plastic epoxy waste from recycling, among which, the method the most researchers engaging in is to add non-materials into plastics to produce composite materials[28-30]. Zheng[28] et al studied the effect on performance of polypropylene by adding nonmetallic materials, from which the result showed that the tensile strength, tensile modulus, curving strength, curving modulus, impact strength against low temperature are able to reach an increase up to 16.3%, 41.5%, 63.5%, 100%, 45.7% respectively.

5. Pyrolysis technique

The pyrolysis technique is mainly used in the process for pyrolysis of the residue after metal recycling, which turns resin plastics into gas or liquid fuels[1]. In Qiu's research, under the conditions of the pyrolysis temperature (400 ~ 550 ℃), heating rate (15 ~ 20 ℃ / min), vacuum degree (pressure 15 kPa) and the thermal insulation time (30 min), the main components of pyrolysis oil in the nonmetallic materials from circuit boards is phenolics with a total content of 84.08%, of which 15.34% is bromine compound [31]. Conditions in techniques, methods an equipment for applying pyrolysis techniques in the recycling of nonmetallic materials are immature, recycling efficiency is low and effective control over the toxic and harmful substances in the waste produced in the process of pyrolysis is still in lack[1].

6. Conclusions

At present, the recovery of the wasted PCB mainly uses the physical technique, which mainly focuses on turning the wasted PCB into powder as fillers or modifying agents in the application of various fields. By applying physical method, cost of materials can be saved, which is in line with demands from energy-efficiency society. As the most potential approach for recycling, research on physical techniques in future mainly fixes on appraisal on environmental risk of application of composite materials in production and application. The pyrolysis technique needs high-level equipment and a large scale of investment, and its products are low in economic value. Although supercritical techniques and solution recovery techniques have little pollution to the environment, they still have such disadvantages as low efficiency, high technical difficulties and investment cost, therefore, the two techniques are still in the phase of laboratory research; energy recovery technique, simple in process, able to substitute for some fuel, is the main technique for recycling nonmetallic materials from waste circuit boards.

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